

BIMATERIALS

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PROPERTIES OF CALCIUM PHOSPHATE POWDER SYNTHESIZED FROM CALCIUM ACETATE AND SODIUM HYDROPHOSPHATE

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The properties of powder synthesized from calcium acetate and sodium hydrophosphate with the ratio $[Ca^{2+}]/[PO_4^{3-}]$ of the starting reagents equal to 1 have been investigated. After synthesis brushite, monetite, and octacalcium phosphate were found in the powder. A substantial mass loss, equal to 26%, on heating is due to not only the decomposition of the phases found but also the removal of the byproducts, consisting of sodium acetate and acetic acid and present in the powder, of the reactions occurring when the solutions of the starting substances interact. After firing at temperatures above 900°C the phases $\beta\text{-Ca}_2P_2O_7$, $\beta\text{-Ca}_3(PO_4)_2$, and $Ca_{10}Na(PO_4)_7$ are found in the samples.

Key words: brushite, monetite, octacalcium phosphate, calcium pyrophosphate, tricalcium phosphate, double calcium sodium phosphate, thermal conversion of calcium phosphates, ceramic composite material.

Synthetic calcium phosphate (CP) powders are the starting product for obtaining inorganic composite materials for bone implants. Chemical deposition from solutions is a convenient and widely used method for synthesizing such powders. CP powders are used to obtain various materials (ceramics, cement, and filled polymers) which are in turn used as preparations for healing bone defects.

Materials for bone implants must possess together with biocompatibility and bioactivity bioreactivity (resistance to dissolution in the body) or bioresorbability (capability of gradually and completely dissolving in the body as the new bone grows) depending on the treatment method used. CP based materials possess superb biocompatibility, which is due to the fact that their chemical composition is identical to that of bone tissue. Many studies of these materials show that they are bioactive, which is determined by the capability of the material to give rise to the formation of hydroxyapatite on its surface in *in vitro* tests in model liquids, whose composition is similar to that of intertissue liquid in the body. Among CP-based materials HAP, containing 100% hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, shows the greatest bioresistance. The following materials can be used as the biodegradable phase in inorganic materials: CP with ratio $Ca/P < 1.67$;

double alkali metal – calcium phosphates; glass in the system $CaO - P_2O_5 - X_2O$ or $CaO - P_2O_5 - SiO_2 - M_2O$, where $M = Na, K$; and, calcium carbonate $CaCO_3$ or calcium sulfate $CaSO_4$.

Materials containing tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) as the resorbable phase have been studied in greatest detail [1, 2]. A number of articles are devoted to the study of materials containing as the resorbable phase calcium pyrophosphate $Ca_2P_2O_7$ (CPP) or the mixture CPP/TCP [3, 4]. A source of the phase CPP in ceramic composite material is glass in the system $CaO - P_2O_5$ [3] or calcium phosphate with the ratio $Ca/P = 1$ (brushite $CaHPO_4 \cdot H_2O$, monetite $CaHPO_4$) [4, 5]. On heating brushite becomes monetite ($T = 200^\circ C$), and monetite becomes CPP ($T = 450^\circ C$).

Previous works have examined the production of ceramic from HAP powders synthesized from different pairs of precursors, such as calcium nitrate and ammonium hydrophosphate [6], calcium chloride and sodium hydrophosphate [7], calcium acetate and potassium hydrophosphate [8], calcium chloride and potassium hydrophosphate [9], and calcium acetate and sodium hydrophosphate [10]. Ceramic has also been obtained from brushite or monetite powders synthesized from ammonium hydrophosphate and calcium nitrate, chloride, and acetate [5], calcium acetate and potassium hydrophosphate [11], and calcium chloride and potassium hydrophosphate [12]. The synthesized powders can

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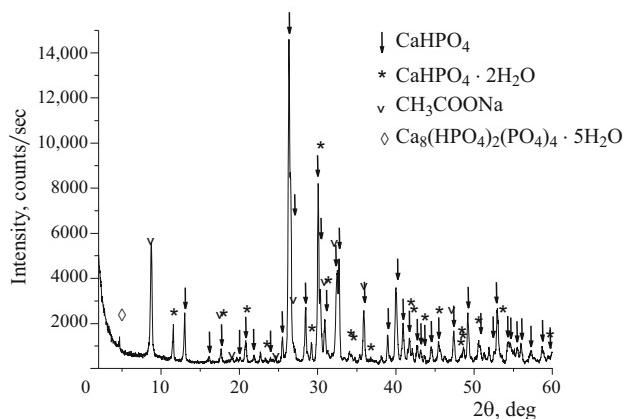


Fig. 1. XPA of synthesized powder (Rigaku D/Max-2500 diffractometer, CuK_α radiation).

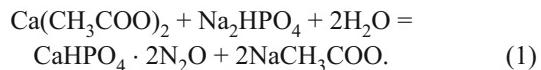
contain substantial amounts of byproduct, which on heating can function as a sintering additive giving rise to the formation of a liquid phase, or react with HAP, forming calcium-sodium or double calcium-potassium phosphates [13]. In obtaining a ceramic from CP powders with ratio Ca/P = 1, which contain as the byproduct a compound of alkali metal, double alkali metal — calcium phosphates can also be expected to form.

In order for a biocompatible phase based on double calcium-sodium phosphates (renanite NaCaPO₄ or Ca₁₀Na(PO₄)₇) to form on heating CP must interact with sodium salt. It has been found that when CP is synthesized from calcium acetate and ammonium hydrophosphate with ratio [Ca²⁺]/[PO₄³⁻] = 1 without pH regulation calcium-deficient HAP is formed (Ca-HAP), which on heating becomes β-TCP [5]. There have been no reports about the properties of CP powder with [Ca²⁺]/[PO₄³⁻] = 1 containing as the byproduct sodium acetate or about obtaining a ceramic based on such powder. When calcium phosphates and NaCH₃COO are heated, calcium carbonate, possessing a relatively low melting temperature, and double sodium – calcium phosphates can form (RF patent RU 2372891 C2, 20.11.2009) [10]. The presence of a melt facilitates the formation of a multiphase bioresorbable ceramic composite material containing a TCP phase and double sodium-calcium phosphates.

The aim of the present work was to study the properties of CP powder synthesized from calcium acetate and sodium hydrophosphate with the ratio [Ca²⁺]/[PO₄³⁻] of the starting reagent equal to 1, and containing sodium acetate as the byproduct of synthesis. To optimize the parameters of the firing stages when obtaining ceramic materials from such mixtures it is important to study the processes occurring during heating.

CP powder with starting reagent ratio [Ca²⁺]/[PO₄³⁻] = 1 was synthesized using water solutions. A 1 liter 0.5 M sodium hydrophosphate solution was added to a 1 liter 0.5 M solution of calcium acetate. The solutions were combined at

room temperature, adding beforehand 1 M acetic acid to the prepared calcium acetate solution:

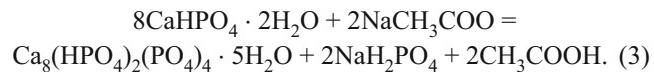


As a result of the reaction (1) sodium acetate accumulates in the solution. Together with pre-added acetic acid the sodium acetate forms a buffer system that maintains the pH level of the reaction mixture at about 5. Such a pH made it possible for the reaction (1) to proceed.

After a precipitate formed the calcium phosphate suspension was heated in the mother liquor to 80°C and held at this temperature for 30 min to convert the brushite into monetite via the reaction



It is known that brushite can be converted into monetite by heating the brushite powder at 200°C and by holding the brushite in a water suspension at 80°C. In addition, for the prescribed values of the pH and temperature the competing reaction of hydrolysis of brushite (and, possibly, monetite) to octacalcium phosphate OCP (Ca₈(HPO₄)₂(PO₄)₆ · 5H₂O) can occur via the reaction



The XPA data for the powder obtained show that the conversion of brushite into monetite after allowing the precipitate to stand did not go to completion, and in addition OCP impurity was found as a peak in the diffraction pattern at 4.8°C (Fig. 1). Thus, the obtained power contains as the main phases brushite and monetite as well as the impurity phases OCP and the byproduct of the reactions (1) and (3) — sodium acetate, sodium dihydrophosphate, and acetic acid.

The precipitate obtained was separated from the mother liquor on a paper filter in a Buechner funnel using a water-jet pump. Next, the precipitate was allowed to dry in a thin layer for two days. The dried precipitate was disaggregated in a planetary mill for 5 min in acetone with the ratios acetone : powder : spheres = 1 : 1 : 5. Next, after the acetone evaporated the powder was passed through a sieve with 200 μm cells. The samples were pressed under pressure 100 MPa in the form small rods 10 × 5 × 3 mm, after which they were fired at different temperatures in the interval 700 – 1300°C with 6-h soaking at the final temperature (heating rate 5 K/min).

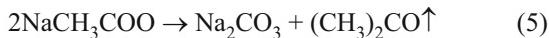
According to the XPA data (see Fig. 1) the synthesized powder consisted of a mixture of monetite, brushite, and OCP as well as a byproduct consisting predominately of sodium acetate. Aside from sodium acetate the accompanying product contained acetic acid, used in synthesis to regulate the pH. This accompanying reaction product is removed during drying and storage of the powder, as is indicated by the

characteristic odor of the synthesized CP powder. The presence of an appreciable amount of accompanying products of the reaction is explained mainly by their adsorption on the surface of the synthetic CP particles. The content of the adsorbed accompanying reaction product, consisting of a mixture of sodium acetate and acetic acid, was found to be 20–26%.

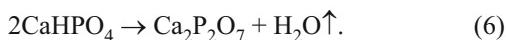
According to thermal analysis (Fig. 2) the total mass loss at 1100°C was 20%. The mass loss of samples after firing at 1200°C in period of 6 h was 26%. The powder mass decreased on heating because of the loss of adsorbed water and acetone, decomposition of some residual amount of brushite via the reaction



at temperature near 200°C, decomposition of sodium acetate via the reaction



to temperature 400°C, transition of monetite into CPP in the interval 400–450°C



The mass loss in the interval 450–1100°C did not exceed 1.5% and could have been due to the decomposition of sodium carbonate — reaction (5). The main loss of mass occurs as a result of the decomposition of the byproduct. The step which would correspond to the reaction (6) on the mass loss curve is expressed indirectly. A peak can be seen in the DTA curve in the interval 400–450°C; this peak reflects the transition of monetite into CPP.

The maximum size of the particle aggregates in the synthesized powder after aggregation (Fig. 3) was 89 μm. The most likely size of the aggregates is 7.6 μm. Scanning electron microscopy showed that the size of the individual crystallites does not exceed 100–150 nm. The particles were plate-shaped. The bulk density of the powder was 0.37 g/cm³, and the density of the compact was 1.63 g/cm³.

According to the dilatometric data (Fig. 4), to 700°C the relative change of the length of the sample did not exceed 0.5%. On heating from 700 to 800°C the shrinkage was 3%. The shrinkage reached 5% after soaking at 800°C for 15 min. Hypothetically, a eutectic melt, one component of which is Na₂CO₃, forms at 800°C. The melting temperature of Na₂CO₃ is 852°C. In the interval 650–600°C, an abrupt change of length is observed on cooling; this length change could be due to the crystallization of the melt. The subsequent course of the curve indicates the usual decrease of the sample size on cooling. The total shrinkage after measurement was 6.75%.

Isothermal soaking was used to investigate the mass losses, shrinkage, and change of the phase composition of the samples. It was determined that the greatest mass loss

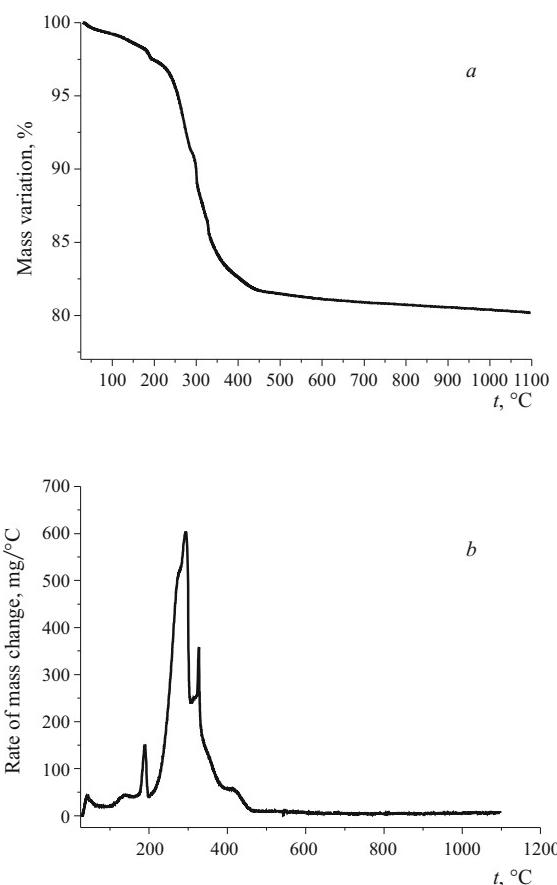


Fig. 2. Integral (a) and differential (b) curves of the change of the mass of the powder containing the byproduct of the reaction (heating rate 10 K/min).

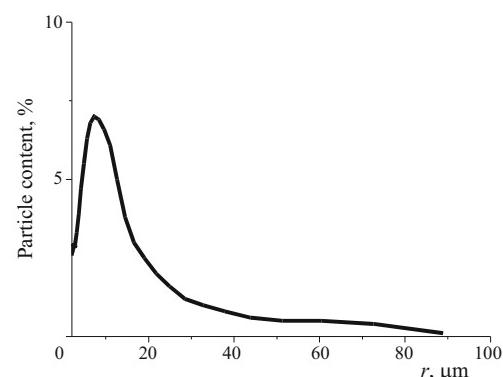


Fig. 3. Particle size distribution by dynamic light scattering method after synthesis and disaggregation (Fritsch Analysette-22 device, Germany).

(26%) is observed after firing at 1200°C. The temperature dependence of the shrinkage (Fig. 5) is nonlinear. The shrinkage reaches 16/5% in the interval 800–900°C, which, evidently, is a result of densification due to the formation of melt, hypothetically, in the system Na₂CO₃–CaO–P₂O₅.

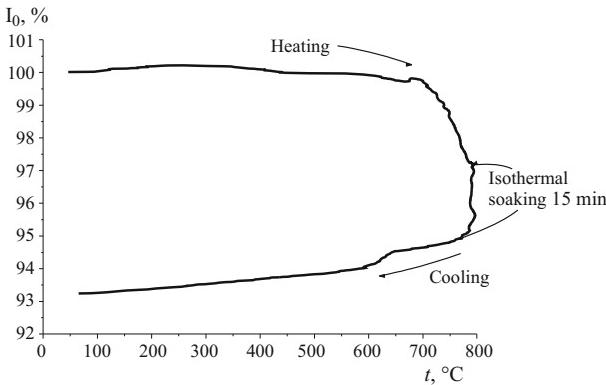


Fig. 4. Dilatometric curve for a sample on heating and cooling with heating rate 5 K/min, soaking time 15 min at $T = 800^\circ\text{C}$ (mechanical quartz dilatometer, equipped with a LIR-14.000 linear displacement sensor, St. Petersburg, Russia).

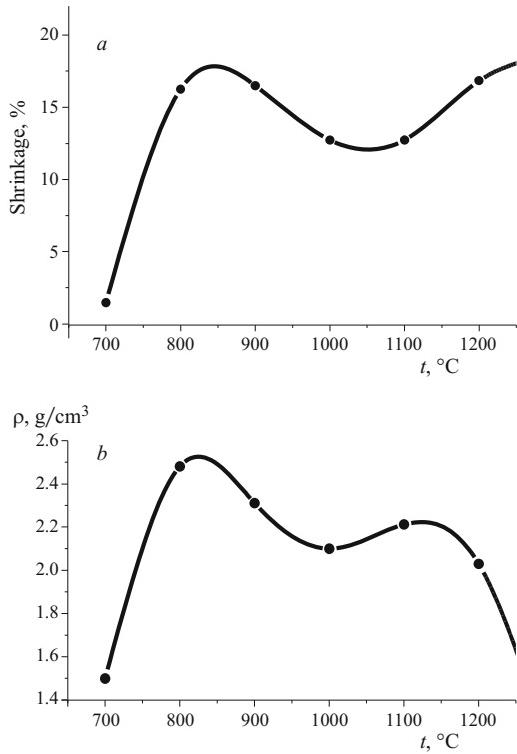


Fig. 5. Linear shrinkage (a) and density (b) versus temperature when studying samples by isothermal soakings.

The shrinkage was 12.5% at 1000°C . The increase of the dimensions of the samples at this temperature is, evidently, due to the decomposition of sodium nitrate and release of CO_2 . As the firing temperature increases to 1200°C the shrinkage once again increases to 18.5%. The density of the samples increases up to temperature 800°C and then decreases non-linearly, reaching 2.0 g/cm^3 at 1200°C .

Figure 6 shows the microstructure of a ceramic after firing at 1200°C . The material is porous, and the pores are

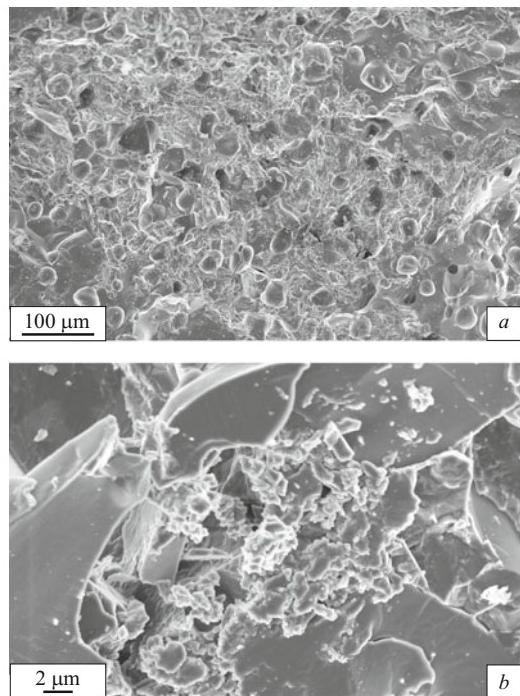
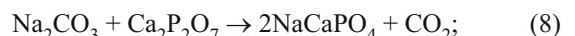
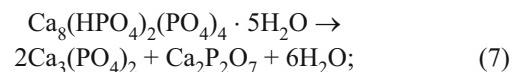


Fig. 6. Microstructure of a ceramic obtained from powder containing sodium acetate after firing at 1200°C for 6 h (scanning electron microscope LEO SUPRA 50VP, Carl Zeiss, Germany).

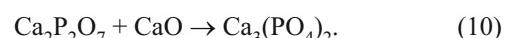
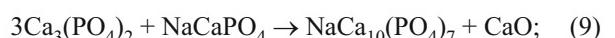
rounded and 20 – 30 μm in size. Grain clusters not exceeding 1 μm as well as grain fragments much large than 2 μm can be seen under higher magnification.

The XPA data (see Table 1) show that with firing to 900°C β -CPP, renanite NaCaOP_4 , and calcium orthophosphate $\text{Ca}_3(\text{PO}_4)_2$ (evidently in the form of sodium-doped orthophosphate $\text{Ca}_{10}\text{Na}(\text{PO}_4)_7$ with β -CPP structure) are found in the material. Above 1000°C β -TCP and β -CPP are present in the material. The XPA data show that chemical reactions resulting in the formation of calcium orthophosphate or double sodium-calcium orthophosphate (renanite) occur in the samples containing CPP, sodium salt, and melt. Hypothetically, the formation of double-phosphate phases can be described by the reactions:

to 800°C :



above 1000°C :



Among the materials participating in the transformations (reactions (6) and (8)), one participant is assumed to be cal-

TABLE 1. Phase Composition of Material after Firing at Different Temperatures

Firing temperature, °C	Phase found*		
	Ca ₂ P ₂ O ₇	Ca ₃ (PO ₄) ₂ (NaCa ₁₀ (PO ₄) ₇)	NaCaPO ₄
800	+	+	+
1100	+	+	-
1300	+	+	-

* +) phase present; -) phase absent.

cium oxide, which was not determined by XPA. However, the data from dilatometry and photomicrography indicate that the interaction in the powder system occurs with the participation of melt, which presumably contains sodium carbonate (sodium oxide), phosphorus oxide, and calcium oxide.

In summary, calcium phosphate powder synthesized from calcium acetate and sodium hydrophosphate with ratio [Ca²⁺]/[PO₄³⁻] = 1 in the presence of acetic acid, containing sodium acetate as the reaction byproduct, is characterized by a collection of various competing chemical reactions resulting ultimately in the formation of a multiphase material. Because of the formation of a melt in the experimental powder system the ceramic based on it can be fired at a lower temperature. The phases TCP, CPP, and double calcium phosphate NaCa₁₀(PO₄)₇ formed as a result are biocompatible and biodegradable. The ratio TCP/CPP in the final material is determined by the ratio OCP/brushite(monetite) in the precipitate. The latter is determined by the rates of the main (1) and competing (3) reactions. The rate of the main brushite crystallization reaction is quite high even at room temperature, while the rate of the competing hydrolysis reaction (3) depends strongly on the temperature and reaches appreciable values at temperatures above 60°C. Therefore the temperature of solution synthesis is one of the key parameters determining the quantitative phase composition of the final multiphase material.

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REFERENCES

1. M. M. Stevens, "Biomaterials for bone tissue engineering," *Materials Today*, **11**(5), 18–25 (2008).

2. <http://us.synthes.com>
3. M. N. Safina, T. V. Safronova, and E. S. Lukin, "Calcium phosphate based ceramic with low sintering temperature and a resorbable phase," *Steklo Keram.*, No. 7, 19–24 (2007); M. N. Safina, T. V. Safronova, and E. S. Lukin, "Calcium phosphate based ceramic with a resorbable phase and low sintering temperature," *Glass Ceram.*, **64**(7–8), 238–243 (2007).
4. T. V. Safronova, V. I. Putlyaev, M. A. Shekhirev, and A. V. Kuznetsov, "Composite ceramic containing a bioresorbable phase," *Steklo Keram.*, No. 3, 31–35 (2007); T. V. Safronova, V. I. Putlyaev, M. A. Shekhirev, and A. V. Kuznetsov, "Composite ceramic containing a bioresorbable phase," *Glass Ceram.*, **64**(3–4), 102–106 (2007).
5. T. V. Safronova, A. V. Kuznetsov, S. A. Korneichuk, et al., "Calcium phosphate powders synthesized from solutions with [Ca²⁺]/[PO₄³⁻] = 1 for bioresorbable ceramics," *Cent. Eur. J. Chem.*, **7**(2), 184–191 (2009).
6. T. V. Safronova, M. A. Shekhirev, V. I. Putlyaev, and Yu. D. Tretyakov, "Ceramic materials based on hydroxyapatite synthesized from solutions with different concentration of the initial reagents," *Neorg. Mater.*, No. 8, 1005–1014 (2007).
7. T. V. Safronova, M. Yu. Steklov, V. I. Putlyaev, and M. A. Shekhirev, "Na-Substituted Ca-deficient carbonatehydroxyapatite for obtaining ceramic materials," *Konstr. Kompozit. Mater.*, No. 4, 34–39 (2006).
8. T. V. Safronova, S. A. Korneichuk, V. I. Putlyaev, and O. V. Boitssova, "Ceramic based on calcium hydroxyapatite synthesized from calcium acetate and potassium hydrophosphate," *Steklo Keram.*, No. 4, 19–24 (2008); T. V. Safronova, S. A. Korneichuk, V. I. Putlyaev, and O. V. Boitssova, "Ceramic made from calcium hydroxyapatite synthesized from calcium acetate and potassium hydrophosphate," *Glass Ceram.*, **65**(3–4), 131–135 (2008).
9. T. V. Safronova, M. A. Shiryaev, V. I. Putlyaev, et al., "Ceramic based on HAP synthesized from calcium chloride and potassium hydrophosphate," *Steklo Keram.*, No. 2, 23–26 (2009); T. V. Safronova, M. A. Shiryaev, V. I. Putlyaev, et al., "Ceramic based on HAP synthesized from calcium chloride and potassium hydrophosphate," *Glass Ceram.*, **66**(1–2), 66–69 (2009).
10. T. V. Safronova, A. V. Kuznetsov, V. I. Putlyaev, and A. G. Veresov, "Ceramic based on hydroxyapatite synthesized from calcium acetate and ammonium hydrophosphate," *Perspekt. Mater.*, Special No. 6, 96–99 (2008).
11. S. A. Korneichuk, T. V. Safronova, V. I. Putlyaev, et al., "Ceramic resorbable materials, containing double potassium-calcium phosphates," *Perspekt. Mater.*, Special No. 6, 91–95 (2008).
12. M. A. Shiryaev, T. V. Safronova, V. I. Putlyaev, et al., "Materials based on calcium phosphate powders containing KCl," *Perspekt. Mater.*, Special No. 6, 20–24 (2008).
13. T. V. Safronova, "Phase composition of ceramic based on calcium hydroxyapatite powders containing accompanying products of the synthesis reaction," *Steklo Keram.*, No. 4, 21–24 (2009); T. V. Safronova, "Phase composition of ceramics based on calcium hydroxyapatite powders containing synthesis by-products," *Glass Ceram.*, **66**(3–4), 136–139 (2009).